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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR THE PREPARATION OF 2-CHLORO-1,1,1,2,3,3,3-  
HEPTAFLUOROPROPANE

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Abstract:

Process for the preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane

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The invention relates to a process for the selective preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane, wherein 1,1,1,2,3,3,3-heptafluoropropane is reacted in the gas phase with elementary chlorine in the presence of high-energy radiation at reaction temperatures in the range of from  $-30^{\circ}$  to  $+500^{\circ}\text{C}$ .

The present invention relates to a process for the selective preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoro-propane ("2-chloro-heptafluoropropane") by photochlorination of 1,1,1,2,3,3,3-heptafluoropropane ("2H-heptafluoropropane").

2-Chloro-heptafluoropropane (boiling point  $-2^{\circ}\text{C}$ ) belongs to the category of the completely halogenated alkanes, which is distinguished by exceptional thermal and chemical stability, non-flammability and special electrical and other physical properties. 2-Chloro-heptafluoropropane can be employed, inter alia, as a coolant or heat transfer medium, as an inert solvent or cleaning agent for low temperature use, as a gaseous or liquid inert medium, for example as a dielectric or insulating medium, as a fire-extinguishing agent or additive to fire-extinguishing agents, or as an etchant for silicon dioxide layers on silicon. In the patent literature, 2-chloro-heptafluoropropane has been proposed as a blowing agent or blowing agent component (U.S. Patent 4,057,973), and for the preparation of soluble, fusible polymers of low flammability from more easily flammable polymers by irradiation (German Patent 1,213,117). Accordingly, there is considerable interest in a simple and economical process, which does not pollute the environment, for the preparation of the compound shown in the title.

2-Chloro-heptafluoropropane has already been described repeatedly in the literature. Most processes for its preparation are based on the fluorination



of a  $C_3$ -compound:

Thus, according to U.S. Patent 2,466,189, the compound  $CF_3CClFCH_2CF_3$  can be obtained by fluorinating 2-chloropentafluoropropene with hydrogen fluoride and lead dioxide in an autoclave, whilst according to British Patent 839,034 it can be obtained by an addition reaction of elementary fluorine with 2-chloropentafluoropropene. The fluorination of 1,1,1-trifluoro-2-chloropropene by means of cobalt trifluoride, in accordance with U.S. Patent 2,670,387 also produces 2-chloroheptafluoropropane, in low yield.

The fluorination of 3-chloro-prop-2-ene with hydrogen fluoride at temperatures above  $500^{\circ}C$ , in accordance with the process of U.S. Patent 3,047,641, results in a yield of about 50% of the title compound. According to U.S. Patent 2,831,035, the reaction of fluorine or of chlorine trifluoride with  $CF_3CCl_2CClF_2$  or  $CF_3CCl_2CCl_2F$  in the presence of an aluminum fluoride catalyst results in the formation of not only octafluoropropane but also 2-chloro-heptafluoropropane.

On a laboratory scale, the title compound can be prepared in yields of over 80% by an addition reaction of chlorine fluoride with hexafluoropropene (D. D. Moldavski, V. G. Temchenko et al., Zh. Org. Khim. 9, 673). However, transfer of this process to an industrial scale is difficult, since by-products which are difficult to separate off are formed and the chlorine fluoride employed is highly toxic, is awkward to handle, since, for example, it reacts vigorously with glass and

explosively with hydrogen-containing compounds, and must, furthermore, in its turn be prepared from elementary fluorine and chlorine.

None of the known processes is suitable for the selective preparation of 2-chloro-heptafluoropropane in high yields. In all the processes, fragmentation reactions or other competitive reactions occur to a considerable degree. The undesired by-products reduce the yield and make extensive distillation operations necessary. Furthermore, the known methods of preparation require starting compounds which are difficult to obtain, uneconomical fluorinating agents or high reaction temperatures, which result in increased corrosion of the reactor materials and short lives of catalysts.

Accordingly, there existed the problem of providing a simple process for the selective preparation of 2-chloro-heptafluoropropane, which is based on easily accessible starting materials and proceeds with high yields.

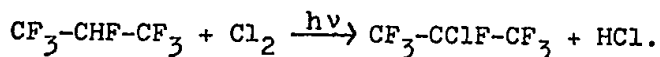
This problem is solved by the invention defined in the main claim.

The process according to the invention can be operated continuously in the manner of conventional gas/gas reactions. A solid catalyst is not required for this purpose. The preferred temperature range is from 20 to 450°C, especially from 30 to 400°C, and more particularly from 40 to 350°C.

High-energy light means, in the present context,

radiation which is capable of decomposing chlorine molecules into chlorine atoms, in particular visible light and ultraviolet light in the range of from 450 to 260 nm. The process according to the invention

5 can be described by the equation



The reaction can be carried out in a conventional irradiation apparatus, such as is used, for example, for chlorinating toluene to give benzyl  
10 chloride. Such an apparatus consists, for example, of a glass flask into which a mercury high-pressure immersion lamp provided with a quartz tube is introduced. The glass flask is additionally equipped with a gas inlet tube, an internal thermometer, a condenser  
15 which is cooled with carbon dioxide, and a drainage stopcock attached to the bottom. The glass flask should be capable of being externally heated at the level of the immersion lamp and at the level of the drainage stopcock.

20 In general, the metered gaseous starting products are introduced as a mixture into the glass flask. The gas mixture leaving the reactor is washed with water, whereby hydrogen chloride formed is absorbed. Thereafter, the residual chlorine is removed with thio-  
25 sulfate solution and dilute sodium hydroxide solution and the product is dried by means of towers which are filled with calcium chloride or with phosphorus pentoxide. The crude product can be condensed in suitable cold traps.

The boiling points of starting materials and end products are summarized in the table below:

Product or material	Formula	Molecular weight	Boiling point/ 1 bar
2H-Heptafluoropropane	$\text{CF}_3\text{CHF}\text{CF}_3$	170.03	$-18^\circ\text{C}$
5 Chlorine	$\text{Cl}_2$	70.96	$-34.1^\circ$
Hydrogen chloride	$\text{HCl}$	36.46	$-85^\circ$
2Cl-Heptafluoropropane	$\text{CF}_3\text{CCl}\text{FCF}_3$	204.47	$-2^\circ$

The 2H-heptafluoropropane employed is of technical-grade purity and is advantageously anhydrous, ie. it is preferably dried with phosphorus pentoxide. 2H-Heptafluoropropane is easily obtainable by the quantitative addition reaction of hydrogen fluoride with hexafluoropropene, for example in accordance with German Offenlegungsschrift 2,712,732. Chlorine is taken from a commercial steel cylinder and is advantageously employed in the anhydrous form, ie. it is dried with, for example, concentrated sulfuric acid.

The conversion of 2H-heptafluoropropane at  $300^\circ$  and atmospheric pressure is about 0.1 to 3 moles/l of reactor volume per hour, depending on the radiation intensity. Lower throughputs are readily achievable. At higher pressures, the conversion can be correspondingly higher. In general, the chlorine is added without dilution; the amount of chlorine is in general between 0.1 and 3.5 moles/l of reactor volume per hour. The amount of chlorine should be at least equivalent to the amount of 2H-heptafluoropropane, which is added simultaneously

and continuously. A slight excess of chlorine is preferred. The molar ratio of 2H-heptafluoropropane/chlorine is, for example, between 1 : 1.5 and 1 : 1, preferably between 1 : 1.15 and 1 : 1.05. Quantitative conversion of 2H-heptafluoropropane can be achieved by using an excess of chlorine. Whilst larger excesses of chlorine are feasible, they are not advantageous, since, if an efficient condenser is used, there is the danger that unconverted chlorine liquefied in the condenser and flowing back into the irradiation reactor may lower the temperature in the reactor and accordingly lead to a reduction in the rate of reaction. Furthermore, the excess of chlorine increases the effort entailed in working up by distillation. Any major excess of chlorine is advantageously removed from the gaseous reaction products by fractional distillation; the recovered chlorine can be re-used. Whilst it is possible to employ a less than equivalent amount of chlorine, this reduces the conversion and increases the effort entailed in working up.

In general, the process is carried out without addition of an inert gas. Whilst dilution with an inert gas, such as, for example, nitrogen, is feasible, it does not offer any significant advantages.

The irradiation reaction can be carried out over a wide temperature range, of from  $-30^{\circ}$  to  $+500^{\circ}\text{C}$ ; however, the reaction proceeds only slowly in the range of from  $-30^{\circ}$  to  $+40^{\circ}\text{C}$ . Accordingly, temperatures above  $40^{\circ}\text{C}$  are preferred. Whilst temperatures in the



range of from 350 to 500°C are feasible they are disadvantageous from the point of view of energy consumption.

5       The residence time of the starting materials  
and of the end products in the reactor is not critical;  
it can, for example, vary between a few seconds and a  
few minutes, without the composition of the crude products being adversely affected by the occurrence of  
side-reactions or secondary reactions.       On the other  
10   hand, economical considerations impose an upper limit  
on the residence time.       Accordingly, it is advantageous, for a high space-time yield, that the reaction  
products formed should be removed from the reactor as  
promptly as possible.

15       The hydrogen chloride formed is in general discharged at the top, through a condenser cooled with  
solid carbon dioxide.       The 2-chloro-heptafluoropropane formed, which collects at the bottom of the  
reactor, can also be taken off continuously, through a  
20   stopcock.

      The process according to the invention is in  
general carried out under atmospheric pressure, but the  
use of reduced pressure or superatmospheric pressure  
(for example up to 10 bar, preferably up to 3 bar) is  
25   also possible, within wide limits.       In order to  
achieve high space-time yields, it is preferred to use  
superatmospheric pressure.

      For reactions on an industrial scale, a continuous and uniform method of operation is desirable.       In

the process according to the invention, continuous introduction of chlorine and 2H-heptafluoropropane, continuous conduct of the reaction, continuous discharge of the reaction products and continuous working up are readily possible. Further particular advantages of the continuous procedure are the improved utilization of the starting materials and the small amount of effluent and waste gas produced.

In the process according to the invention, the conversion of 2H-heptafluoropropane is in general above 90% and often above 99%.

Because of the high selectivity of the process according to the invention, the yields of 2-chloro-heptafluoropropane are also above 90% and often above 98% of theory. The 2-chloro-heptafluoropropane produced is obtained in high purity. Working up is therefore extremely simple.

In view of literature statements concerning the lack of reactivity towards chlorine of hydrogen atoms in the immediate vicinity of trifluoromethyl groups, it is surprising that the substitution of hydrogen by chlorine in 2H-hexafluoropropane proceeds so smoothly in the process according to the invention.

It is known that in comparable compounds such as  $\text{CF}_3\text{-CH}_2\text{-CF}_3$  and  $\text{CF}_3\text{-CH}(\text{CCl}_3)\text{-CF}_3$ , hydrogen is not replaced by chlorine (Houben-Weyl, Methoden der organischen Chemie (Methods of Organic Chemistry), 1962, volume V/3, pages 594-598).

The process is illustrated by the Examples which follow.

Example 1

The experimental arrangement consists of a  
5 multi-neck irradiation flask made of <sup>®</sup> DURAN glass,  
which has a capacity of 2 liters and into which an  
ultraviolet high-pressure mercury immersion lamp pro-  
vided with a thin-walled quartz glass tube is intro-  
duced. The irradiation flask is additionally  
10 equipped with a gas inlet tube, which terminates near  
the immersion lamp, an internal thermometer, which  
extends into the vicinity of the immersion lamp, a con-  
denser filled with solid CO<sub>2</sub>, which is placed on one  
of the ground-glass connections attached to the top,  
15 and a drainage stopcock located at the bottom of the  
irradiation flask. The outer walls can be addition-  
ally heated externally, by means of electrical radiant heaters,  
at the level of the immersion lamp and at the level of  
the drainage stopcock. Both the upper exit of the  
20 condenser and the exit of the drainage cock lead to a  
wash vessel, filled with water, to take up the hydrogen  
chloride formed. These wash vessels are followed by  
wash vessels filled with aqueous 10% strength Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
solution to take up the excess chlorine, and vessels  
25 filled with aqueous 10% strength NaOH for the final  
wash. These are then followed by two drying towers,  
one filled with CaCl<sub>2</sub> for pre-drying and the other  
filled with P<sub>2</sub>O<sub>5</sub> for final drying. The gaseous crude  
product is finally condensed in a high-efficiency cold

trap, cooled with  $\text{CO}_2$ .

Elementary chlorine is taken from a commercial steel cylinder, dried with concentrated  $\text{H}_2\text{SO}_4$ , metered by means of a flowmeter and mixed with the stream of  
5  $\text{CF}_3\text{CHFCl}_2$  gas.

2H-Heptafluoropropane is prepared in accordance with German Offenlegungsschrift 2,712,732, by hydrofluorination of hexafluoropropene in the presence of a chromium oxyfluoride catalyst. It is dried with  
10  $\text{P}_2\text{O}_5$ , metered by means of a flowmeter and mixed with the stream of  $\text{Cl}_2$ .

Before starting the photochlorination, the reaction chamber, which has beforehand been flushed with  $\text{N}_2$ , is pre-heated by switching on the ultraviolet lamp;  
15 this results in temperatures of about  $150^\circ$  to  $180^\circ\text{C}$  in the reactor chamber. In the immediate vicinity of the immersion lamp, temperatures of  $260^\circ$  to  $300^\circ\text{C}$  are measured on the quartz glass.

To photochlorinate 2H-heptafluoropropane, a total  
20 of 76 g (0.45 mole) of  $\text{CF}_3\text{CHFCl}_2$  and 33 g (0.46 mole) of chlorine, corresponding to a molar ratio of  $\text{CF}_3\text{CHFCl}_2 : \text{Cl}_2$  of 1 : 1.02, is introduced in the course of 2 hours, at temperatures of  $120^\circ$  to  $90^\circ\text{C}$ . During the experiment, the hydrogen chloride evolved which is  
25 not retained by the condenser is absorbed in the wash water receiver. After completion of the reaction, flushing with  $\text{N}_2$  is employed in order to wash the entire hydrogen chloride into the wash water. In the present example (1) the other gaseous reaction products,

which collect at the bottom of the irradiation vessel, are discharged through the drainage stopcock, located at the bottom, only after completion of the reaction.

0.44 mole of HCl is found, by titration, in the wash water; HF is not found. The condensed crude product is examined by gas chromatography on a <sup>®</sup> PORAPAK column. This reveals the following:

	$\text{CF}_3\text{CClFCF}_3$	98.1%
	$\text{CF}_3\text{CHF}_3$	1.7%
10	$\text{CF}_3\text{CClFCClF}_2$	0.1%
	$\text{CF}_3\text{CF}_3$	< 0.05%
	$\text{CF}_3\text{CF}_2\text{CF}_3$	< 0.05%

The two last-mentioned components are unconverted impurities of the heptafluoropropane employed;

15  $\text{CF}_3\text{CClFCClF}_2$  is produced by chlorination of  $\text{C}_3\text{F}_6$ , which is also present in traces in the starting material.

The liquid crude product weighs 88 g. Accordingly the yield of  $\text{CF}_3\text{CClFCF}_3$  is 95.4% of theory, based on  $\text{CF}_3\text{CHF}_3$  converted. The 2-chloro-1,1,1,2,3,3,3-hepta-  
20 fluoropropane is additionally identified by <sup>19</sup>F-NMR measurement, infrared recordings and determination of the boiling point, which is -2°C.

#### Example 2

$\text{CF}_3\text{CHF}_3$  is photochlorinated, at temperatures  
25 of 115° to 110°C at the beginning of the experiment and temperatures of 35° to 20°C at the end of the experiment, by passing into the apparatus of Example (1), in the course of 5.5 hours, a total of 467 g (2.75 moles) of  $\text{CF}_3\text{CHF}_3$  and 198 g (2.79 moles) of  $\text{Cl}_2$ , corresponding

to a molar ratio of  $\text{CF}_3\text{CHF}_3$  :  $\text{Cl}_2$  of 1 : 1.01. The condensed reaction products which collect at the bottom of the irradiation flask are, as in Example (1), removed via the drainage stopcock only after completion of the experiment, and are then washed.

1.84 moles of HCl are found by titration in the wash water of the gases. Analysis by gas chromatography reveals the following composition of the condensed crude product:

10	$\text{CF}_3\text{CClFCF}_3$	67.5%
	$\text{CF}_3\text{CHF}_3$	32.1%
	3 other components each	0.1%

The condensate weighs 512 g. The yield of  $\text{CF}_3\text{CClFCF}_3$  is accordingly 90.5% of theory, based on  $\text{CF}_3\text{CHF}_3$  converted; however, the conversion of  $\text{CF}_3\text{CHF}_3$  is only about 68%.

#### Example 3

A total of 495 g (2.91 moles) of  $\text{CF}_3\text{CHF}_3$  and 217 g (3.06 moles) of chlorine, corresponding to a molar ratio of  $\text{CF}_3\text{CHF}_3$  :  $\text{Cl}_2$  of 1 : 1.05, are introduced as gas, in the course of 5 hours, into the apparatus of Example (1), at temperatures of  $120^\circ$  to  $110^\circ\text{C}$ , which can be maintained over the entire experiment. The reaction products which collect are discharged continuously and uniformly via the drainage stopcock, located at the bottom of the irradiation flask, except for a constantly remaining residual amount of about 10 to 15 ml, and are then washed.

2.76 moles of HCl are found in the wash water of

the gases. Gas chromatography measurements on the collected condensed crude product show the following composition:

5	$\text{CF}_3\text{CClFCF}_3$	95.3%
	$\text{CF}_3\text{CHF}_2$	3.9%
	Remainder: secondary components	0.8%.

The condensate weighs 585 g. Accordingly the yield of  $\text{CF}_3\text{CClFCF}_3$  is 97.6% of theory, based on  $\text{CF}_3\text{CHF}_2$  converted.

10 Example 4

A total of 1,080 g (6.35 moles) of  $\text{CF}_3\text{CHF}_2$  and 526 g (7.41 moles) of chlorine, corresponding to a molar ratio of  $\text{CF}_3\text{CHF}_2 : \text{Cl}_2$  of 1 : 1.17, is introduced, in the course of 7.5 hours, into the apparatus of Example (1), at temperatures of  $135^\circ$  to  $125^\circ\text{C}$ . The outer walls of the flask are additionally heated, at the level of the immersion lamp and of the drainage stop-cock, by means of electrical radiant heaters. As in Example (3), the reaction products which collect are discharged continuously and uniformly from the flask.

6.31 moles of HCl are found in the wash water. Analysis by gas chromatography reveals the following composition of the crude product:

25	$\text{CF}_3\text{CClFCF}_3$	99.7%
	$\text{CF}_3\text{CHF}_2$	0.15%
	$\text{CF}_3\text{CClFCClF}_2$	< 0.02%
	$\text{CF}_3\text{CF}_2\text{CF}_3$	< 0.05%
	$\text{CF}_3\text{CHFCClF}_2$	0.1%

- 15 -

The condensate weighs 1,289 g; accordingly the yield of  $\text{CF}_3\text{CClFCF}_3$  is 99.1% of theory, based on  $\text{CF}_3\text{CHF}_3$  converted. The conversion of  $\text{CF}_3\text{CHF}_3$  is 99.85% of theory.



PATENT CLAIMS

1. A process for the selective preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (I), wherein 1,1,1,2,3,3,3-heptafluoropropane (II) is reacted in the gas phase with elementary chlorine in the presence of high-energy radiation at reaction temperatures in the range of from  $-30^{\circ}$  to  $+500^{\circ}\text{C}$ .
2. A process as claimed in claim 1, wherein (II) is reacted with chlorine in a molar ratio of 1 : 1.0 to 1 : 1.5, preferably of 1 : 1.05 to 1 : 1.15.
3. A process as claimed in claim 2, wherein the reaction temperatures are from  $40^{\circ}$  to  $450^{\circ}\text{C}$ .

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